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(54) A multilayer plain bearing

(57) A multilayer plain bearing comprises a steel support body, preferably a steel support shell, an intermediate layer (1) of lead bronze, i.e. a copper alloy with a lead content of from 8 to 30%, a barrier layer (3) of electrochemically deposited iron or nickel and a bearing layer (4) cast or electrochemically applied to this barrier layer (3), the bearing layer (4) having a tin content of from 8 to 93%.

The lead inclusions (2) at the surface of the intermediate layer (1) are removed by treatment with, eg, a solution of acetic acid and hydrogen peroxide whereafter the surface is ultrasonically cleaned before the barrier layer (3) is applied.

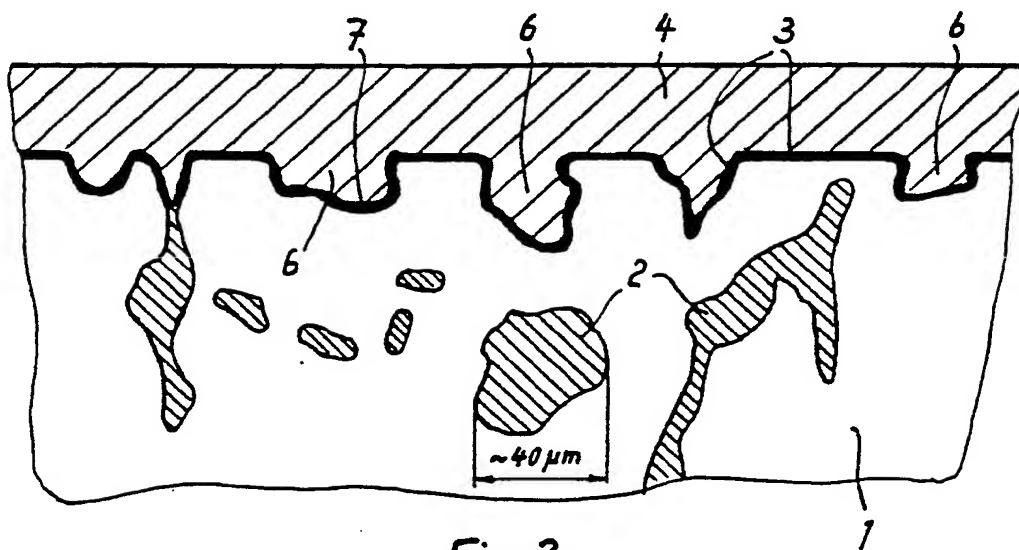
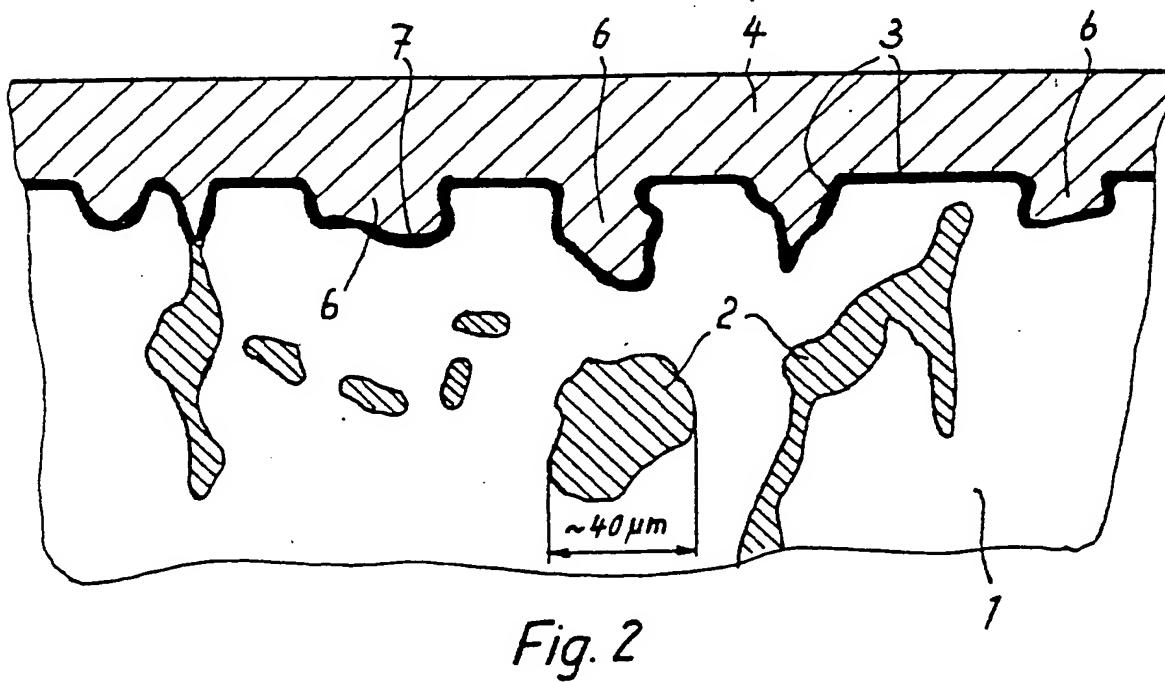
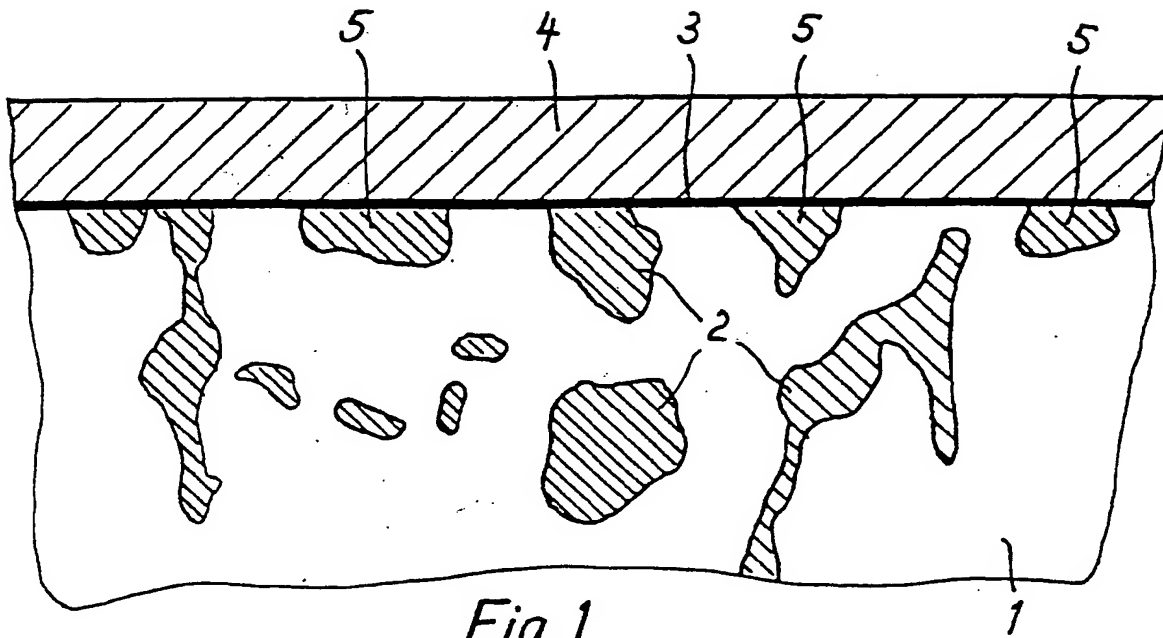


Fig. 2

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SPECIFICATION

A multilayer plain bearing

- 5 The invention relates to a multilayer plain bearing comprising a steel support body, preferably a steel support shell, an intermediate layer of lead bronze, i.e. a copper alloy with a lead content of from 8 to 30%, a barrier layer
- 10 of electrochemically deposited iron or nickel and a bearing layer cast on or electrochemically applied to this barrier layer, the bearing layer having a tin content of from 8 to 93%.

- Plain bearings of the above-mentioned type
- 15 largely satisfy the requirement that at the boundary surfaces of the individual metals no physico-chemical process take place which result in the bonding quality being impaired. Processes of this type can take place when, at
- 20 the boundary surface of two metal layers, chemical elements from different alloys of these layers encounter one another and can react with one another to form compounds which have undesirable properties. These
- 25 compounds are mostly intermetallic phases of extraordinary hardness and brittleness.

- The intermetallic phases Cu_3Sn and Cu_6Sn_5 are especially undesirable, and are formed between copper and tin when a lead bronze is
- 30 used as intermediate layer and an alloy with a tin content is used as bearing layer. The most important alloys with a tin content for bearing technology are white metals, which are applied to the lead bronze in a composite casting process, and also electrochemically applied
- 35 alloys with from 10 to 20% of tin, 2 to 3% copper and the remainder lead. Recently, electrodeposited bearing layers have become more important which have a content of approximately 92% tin and about 7% antimony.
- 40

- To ensure that no reaction can occur between the copper of the lead bronze and the tin of the bearing layer, it is conventional to cover the surface of the lead bronze, prior to
- 45 the application of the tin-containing bearing layer metal, with an electrochemically applied barrier layer of a few micrometres in thickness and then to apply the bearing layer metal onto this so-called barrier. Broadly speaking, in the
- 50 past a nickel barrier proved to be satisfactory for bearings with a galvanic bearing layer having a tin content of from only 10 to 20%.

- However, for bearings with white metal applied by casting, substantial limitations must
- 55 be applied to this nickel barrier. In particular, tin-based white metals, which generally have a tin content of from 80 to 90%, cannot be cast onto a nickel barrier with the requisite bonding quality.

- 60 The reason for this is that although the nickel barrier is probably able to prevent the formation of the extremely dangerous intermetallic phases Cu_3Sn and Cu_6Sn_5 , nickel also forms brittle intermediate compounds with tin.
- 65 The formation rate of these phases is rela-

- tively low if the reaction partners nickel and tin are in a solid state and at a relatively low temperature. For this reason, nickel is a practical barrier layer material for bearings with an electrochemical bearing layer. However, in the
- 70 case of white metal bearings with a bearing layer applied by casting, during the casting process, which takes place at a temperature of between 380 and 420°C, an intermetallic
- 75 layer of Ni_3Sn and Ni_5Sn_2 with a layer thickness of from 1 to 2 micrometres is already formed at the boundary surface between nickel and white metal.

- Under the dynamic loads occurring during bearing operation cracks occur in this brittle intermediate layer, which result in the separation of large areas of the white metal. The formation of the intermetallic layer takes place with particular intensity when tin-based white
- 80 metals are applied by casting. As already mentioned, in these alloys the tin content lies between 80 and 90%. For the sake of completeness, we mention here the fact that the casting of lead-based white metals, which as
- 85 a rule only contain about 10% tin, is less critical in the case of a nickel barrier.

- However, because cast tin-based white metals are superior to lead-based white metals in respect of fatigue strength, corrosion resistance and cavitation resistance, the tin-based
- 90 white metals are naturally of major significance for use as bearing layer materials.

- In the case of the previously mentioned electrochemically deposited bearing layers with
- 100 a high tin content and containing a certain amount of antimony, the risk of brittle intermetallic layers being formed at the boundary surface between nickel and tin during the production of bearings is in fact slight because of the low temperatures. However, in diesel engines with high specific performance, reaction energy is continuously imparted to the bearing
- 105 layer, thus resulting in an elevated diffusion rate so that here too these brittle intermetallic layers are formed, which reduce the service life of bearings. Accordingly, the nickel barrier proves to be only of very limited use also for this bearing layer.

- For decades it has been known that iron and cobalt are also suitable as a barrier between a copper alloy and an alloy with a high tin content. However, for cast bearing layers with a high tin content cobalt has even poorer diffusion stability than nickel. Hitherto it has
- 110 also not been possible to successfully use an iron barrier between lead bronze and a galvanic bearing layer or a cast white metal layer. The main reason for this is that an iron layer deposited on to lead does not have the adhesion strength required for a plain bearing. In particular, it has not been possible hitherto to apply white metal to electrochemically deposited iron barrier layers without the iron becoming separated from the lead bronze. These difficulties are the reason why plain bearings
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with an iron barrier have not been used hitherto, even though iron behaves substantially more favourably with respect to the formation of intermetallic compounds.

- 5 In the case of thin bearing layers with a thickness of only 20 to 50 micrometers, not infrequently it happens that the bearing layer becomes completely worn and the shaft initially runs on the barrier layer and then on the lead bronze. The phase in which the shaft passes through the barrier layer can prove to be critical. In particular, when the barrier layer comprises the nickel hitherto used exclusively as barrier layer metal, it has to be assumed that the barrier layer possesses a very high degree of hardness for the shaft, in particular for a non-hardened shaft. In the case of nickel, this hardness may be up to 380 Vickers units.
- 10 Like nickel, electrochemically deposited iron can also be very hard. This high degree of hardness is mainly brought about by hydrogen dissolved in the iron, which is also deposited during electrochemical iron deposition.
- 15 Therefore, in addition to diffusion stability, the barrier has to have further properties not provided hitherto, which ensure maximum protection against fretting between the shaft and the barrier, which prevents any damage to the shaft surface which could detrimentally affect operating reliability when the shaft passes through this critical component of the substantially ternary structure of the plain bearing layers.
- 20 Thus it would be desirable to provide, in a plain bearing having a high load-bearing capacity, conditions which enable both metals, namely iron or nickel, to be used alternatively in an economical manner as an electrochemically deposited barrier and this barrier to have better compatibility with respect to the counter-rotating surface, for example when the shaft runs directly on the barrier after the bearing layer has worn through.
- 25 According to the invention, the intersected lead components of the copper alloy are removed from the surface of the intermediate layer to be electrochemically treated and the electrochemical barrier layer extends into the cavities of the copper matrix formed in this way and covers the walls thereof in the manner of a lining, the cavities lined by the barrier layer being filled with metal components of the bearing layer.
- 30 A plain bearing of this type according to the invention offers considerable advantages. The surface of lead bronze provided with lead-free cavities can satisfy the requirement that in an economical manner either iron or nickel can be electrochemically deposited as the barrier. Therefore, the required suitable diffusion barrier is available for all conventional bearing layer alloys, both cast and electrochemically deposited. The microfinely fissured surface of lead bronze necessarily results not only in a

substantially enlarged surface area for the strength of the diffusion bonding of the bearing layer on the barrier but also ensures satisfactory anchoring of the bearing layer in the intermediate layer.

- 70 Despite the lining of the cavities with the barrier, sufficient space remains in the recesses of this now electrochemical surface to ensure that the subsequently applied bearing layer projects into this recess. Since the white metal thus pervades, as it were, the barrier layer at numerous microscopically small places, the barrier layer acquires a similar structure to lead bronze, i.e. relatively soft inclusions (here white metal, there lead) are embedded in a relatively hard base material (here iron or nickel, there copper). The proportion of the soft phase in iron or nickel is slightly smaller than in bronze, since a part of the cavity volume is lost because of the barrier layer lining. Therefore, the barrier according to the invention has plain bearing qualities.
- 75 It has been found that a barrier layer thus rendered heterogeneous in its structure has the considerable advantage, in relation to a homogeneous smooth barrier, that even unhardened shafts can pass through these novel barriers without damage to their surfaces. In view of the fact that, as a result of wear, the finely interspersed white metal is exposed, oil wettability is better at these locations and the combined wear behaviour of the barrier layer carrying the shaft is thereby improved. Furthermore, in the event of local overheating in the bearing, the white metal, whose lower melting interval limit is at 235°C, can emerge from the recesses and coat the barrier layer with a thin white metal film which acts so as to reduce friction. The service life of the bearing is considerably increased thereby.
- 80 To ensure that this phase of the shaft passing through the barrier lasts for the shortest possible time, it is preferable for the barrier layer to have a mean thickness of between only 3 and 8 micrometres after electrochemical deposition. The electrochemical times for applying the barrier are thus also brief.
- 85 Multilayer plain bearings, which have a bearing layer of cast tin-bearing alloys, are particularly corrosion and wear-resistant. In the event that, as a result of very fine machining, the thickness of the bearing layer lies in the range of from 0.1 to 0.3 mm, bearings of this type also exhibit a very high degree of fatigue strength. Above all, a prerequisite for this is that the bond between the bearing layer and the intermediate layer via the barrier is of outstanding strength. As already mentioned above, this is achieved in that, in the case of a cast bearing layer comprising a tin alloy with from 5 to 10% antimony, 2 to 5% copper, up to 0.5% arsenic and up to 2% cadmium, an iron layer is provided as the barrier.
- 90 The outstanding bonding strength of the bearing layer to the intermediate layer results

from the fact that in the transition zone into the cast bearing layer this iron barrier layer has a reaction layer of an iron-tin compound (FeSn_2). The manner in which this reaction layer is formed will be explained below.

It is also possible to use as bearing layer a hitherto known electrochemical ternary layer, wherein the bearing layer electrochemically applied to the iron or nickel barrier layer is a bearing alloy with 8 to 15% tin, 0 to 3.5% copper and the remainder lead.

As already mentioned, it has recently become possible for bearing layers with a high tin content to be mass electrochemically deposited, in which case a nickel barrier does not have sufficient diffusion stability. According to the invention, an improvement may be afforded by providing an iron layer as barrier in the case of an electrochemically applied bearing layer comprising a tin alloy with from 3 to 9% antimony, less than 1% copper and less than 0.5% lead. Since this tin electrochemical bearing layer is produced with a layer thickness of up to 50 μm , the heterogeneous structure of the iron barrier proves to be particularly advantageous for the resistance of the bearing to seizure when the barrier layer is penetrated.

A particularly advantageous embodiment of the bearing according to the invention is provided when the cast bearing layers have a thickness of between 50 and 100 μm and the electrochemical bearing layers a thickness of between 10 and 60 μm .

It is generally known that lead can be removed from a surface by treatment with agents such as, for example, acetic acid, formic acid or citric acid. This process makes it possible for the lead of the lead-bronze inclusions to be dissolved selectively, the copper or copper-tin base material not being attacked in practice. In order to produce the described surface of the lead bronze for the bearing according to the invention, it is thus possible to proceed so that the lead components intersected on the surface of the intermediate layer are subjected to treatment with a solution of acetic acid and hydrogen peroxide, subsequently the reaction products thus formed are removed ultrasonically from the cavities and then the barrier layer is electrochemically deposited.

By dissolving the lead inclusions in this way out of the surface of the lead bronze, a cavity or depression open towards the surface is formed at the location of each lead inclusion. The remainder of the lead solvent and solution products has to be completely removed from these cavities before the iron is electrochemically deposited. The removal of these residues may be carried out effectively by ultrasonic action under water. The iron barrier layer is subsequently deposited from one of the conventional hydrochloric or sulphuric electrolytes in a layer thickness of preferably between 2

and 3 micrometres. If it is desired to deposit a nickel barrier instead of an iron barrier, the process long known to the person skilled in the art can be used. These baths generally have sufficient dispersion capacity to ensure that the walls of the cavity are also lined with an electrochemical layer. Because of the multiplicity of lead inclusions there is always a relatively high proportion with a diameter of more than 6 micrometres, these cavities are not completely filled up by the electrochemical layer but are merely reduced by the thickness of the barrier layer. If as a result of the succeeding operation of white-metal application the barrier is covered with white metal, the lined cavities are also filled with this white metal.

In the case in which this barrier surface interspersed with these cavities is to have a white metal cast on to it, then prior to the casting of the white metal it is necessary for the iron barrier layer to be tinned by causing a reaction between molten tin (II) chloride and iron, wherein liquid tin is deposited on the iron surface to form FeSn_2 .

If it is desired to electrochemically deposit the bearing layer onto the barrier layer interspersed with cavities, care has to be taken to ensure that the electrochemical deposition of the bearing layer is effected immediately following the electrochemical deposition of the barrier layer.

If iron is used as the barrier layer metal, it is important for the iron of this barrier layer to be very soft. This can be achieved by heat treatment of the iron barrier layer before application of the bearing layer, wherein the bearing is preferably kept for one hour at between 280 and 300°C.

The present invention is further described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a schematic illustration of a metallographic section through a known plain bearing in accordance with the preamble; and

Figure 2 is a schematic illustration of a metallographic section through a bearing layer and an intermediate layer of a multilayer plain bearing in accordance with the invention.

In the drawings the reference numeral 1 designates a copper matrix in which the lead component 2 is embedded more or less finely divided, spherically or dendritically. During the machining of the lead bronze surface the lead particles 5 present there are intersected so that these lead inclusions are readily visible on the machined surface. In known multilayer plain bearings of this type the diffusion barrier 3 is electrochemically applied to this smooth machined surface, so that both the copper matrix and the intersected lead particles are covered by the barrier. If nickel is used as the barrier material, a substantially closed electrochemical surface is formed, onto which the bearing layer 4 is applied, the barrier prevent-

ing any diffusion of tin from the bearing layer into the lead bronze. If the bearing layer 4 is of white metal which preponderantly contains lead and only very small amounts of tin, the danger of the formation of intermetallic boundary layers at the nickel surface is very slight. However, if it is attempted to cast onto this nickel surface liquid white metals having a high tin content, a brittle intermetallic layer of Ni_3Sn and Ni_3Sn_2 is then formed with a layer thickness of between 1 and 2 micrometres.

However, this diffusion process is by no means terminated with the production of the bearing but continues during operation as a plain bearing until, finally, the entire nickel barrier has dissolved. After this reaction between the bearing layer and the barrier is fully completed, tin diffusion continues through the intermetallic intermediate layer consisting of Ni_3Sn_4 and forms intermetallic compounds with the lead bronze, in particular with the copper. In the early stage of this secondary diffusion cracks are formed in the Ni_3Sn_4 layer so that local areas of the deposited bearing layer are isolated and break away. The formation of this copper-tin-nickel compound reduces quite considerably the bonding strength because of the extreme brittleness of this intermetallic compound. Measurements have shown that a nickel layer originally only 3 micrometres thick at a temperature of 135°C will have increased after only about 3,000 hours to a reaction layer thickness of 6 micrometres.

Figure 2 shows the upwardly open cavities 6 from which lead has been removed and which are substantially lined with the diffusion barrier. In the case of such a surface of the lead bronze which is to be electrochemically treated, it is possible for both nickel and iron to be reliably electrochemically deposited as the barrier. Ultrasonic cleaning can ensure that these cavities are free of any reaction products formed during the removal of the lead inclusions. Therefore, it is also possible to enable the barrier to be deposited with reliability on the bottom of the cavities so that, despite the very jagged surface of the barrier, it is substantially closed. The bearing layer 4 thus forms projections 6 into the lead-bronze cavities which, firstly, ensure satisfactory anchoring of the bearing layer in the lead bronze and, secondly, also represent a surface enlargement for the bonding of the bearing layer on the barrier. It is also clearly evident from Figure 2 that, with a worn bearing layer, the shaft still runs on a considerable percentage of white metal. Moreover, in this wear phase of the bearing, these islands of white metal provide a certain embedding capacity for dirt particles and a certain resistance to seizure in the event of sudden rises in temperature. It can be readily imagined that these "antifriction properties" of the barrier are maintained throughout the wearing period through this barrier. Finally, the shaft runs in a wear stage

of the bearing in which all participating metals, namely bearing layer metal, barrier metal, copper and lead, appear at the surface of the bearing until, finally, after the barrier region has been completely worn through, the shaft runs purely on lead bronze.

CLAIMS

1. A multilayer plain bearing comprising a support body, an intermediate layer of a copper alloy with a lead content of from 8 to 30%, a barrier layer of electrochemically deposited iron or nickel and a bearing layer cast or electrochemically applied to this barrier layer, the bearing layer having a tin content of from 8 to 93%, wherein the intersected lead components of the copper alloy are removed from the surface of the intermediate layer to be electrochemically treated, and the electrochemical barrier layer extends into the cavities of the copper matrix formed in this way and lines the walls thereof, the cavities lined by the barrier layer being filled with metal components of the bearing layer.

2. A multilayer plain bearing according to claim 1, wherein the barrier layer has a mean thickness of from 3 to 8 μm .

3. A multilayer plain bearing according to claim 1 or claim 2, wherein the bearing layer is a cast bearing layer comprising a tin alloy with from 5 to 10% antimony, 2 to 5% copper, up to 0.5% arsenic and up to 2% cadmium, and the barrier layer is of iron.

4. A multilayer plain bearing according to claim 3, wherein in the transition zone into the cast bearing layer the iron barrier layer has a reaction layer of an iron-tin compound.

5. A multilayer plain bearing according to claim 1 or claim 2, wherein the bearing layer applied electrochemically to the iron or nickel barrier layer is a bearing alloy with 8 to 15% tin, 0 to 3.5% copper and the remainder lead.

6. A multilayer plain bearing according to claim 1 or claim 2, wherein the bearing layer is an electrochemically applied bearing layer comprising a tin alloy with from 3 to 9% antimony, less than 1% copper and less than 0.5% lead, and the barrier layer is of iron.

7. A multilayer plain bearing according to any one of claims 1 to 6, which has a cast bearing layer of between 50 and 100 micrometres thick or an electrochemical bearing layer of between 10 and 60 micrometres thick.

8. A method for the production of a multilayer plain bearing according to claim 1, wherein the lead components intersected on the surface of the intermediate layer are subjected to treatment with an agent to selectively remove the lead, subsequently the reaction products thus formed are removed from the cavities and then the barrier layer is electrodeposited.

9. A method according to claim 8 wherein the treating agent is a solution of acetic acid

and hydrogen peroxide.

10. A method according to claim 8 or claim 9 wherein the reaction products are removed ultrasonically.

5 11. A method according to any one of claims 8 to 10 for the production of a multilayer plain bearing according to any one of claims 3, 4 or 7, wherein prior to the casting of the white metal, the Fe-barrier layer has tin applied thereto by causing a reaction between
10 molten tin (II) chloride and iron, whereupon liquid tin is deposited on the iron surface to form FeSn_2 .

12. A method according to any one of
15 claims 8 to 10 for the production of a multilayer plain bearing according to any one of claims 5, 6 and 7, wherein the electrochemical deposition of the bearing layer is effected immediately after the electrochemical deposition
20 of the barrier layer.

13. A method for the production of a multilayer plain bearing according to any one of claims 1 to 7, wherein the Fe-barrier layer is heat treated before application of the bearing
25 layer.

14. A method according to claim 13 wherein the bearing is kept for about one hour at between 280 and 300°C.

15. A method for the production of a multilayer plain bearing as defined in claim 1 and substantially as hereinbefore described.
30

16. A bearing whenever produced by a method according to any one of claims 8 to 15.

35 17. A bearing substantially as hereinbefore described other than with reference to prior art.

18. A multilayer bearing comprising a support body and an intermediate layer of lead—
40 containing copper alloy a surface of which contains cavities left by the removal of the lead inclusions at the surface and has electrochemically deposited thereon an iron or nickel barrier layer which extends into and lines the
45 cavities, and a tin—containing bearing layer being applied to the barrier layer and filling the cavities in the surface of the intermediate layer.

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